Chapter 5

Half-sandwich mono and dinuclear complexes of platinum group metals bearing pyrazolyl-pyridine analogues: Synthesis and spectral characterization

The chelating ligands pp-CI and bppp were synthesized and their reactions with arene ruthenium, Cp* rhodium and iridium dimers resulted in the formation of mono and dinuclear complexes. However reactions with the bppm ligand which is having Pyrimidine Bridge between pyrazolyl-pyridine units resulted only in the formation of mononuclear complexes.

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5.1 Introduction

Mono and binuclear complexes of platinum group metals containing heterocyclic nitrogen based ligands have received considerable attention owing to their catalytic activities\textsuperscript{1-8} and very recently as non-linear optical (NLO) materials\textsuperscript{9,10} as well as in the development of new biologically active agents.\textsuperscript{11-16} The organometallic complexes of \( \eta^6 \)-arene ruthenium,\textsuperscript{17,18} and \( \eta^5 \)-half-sandwich complexes of rhodium and iridium have attracted considerable interest as potential anticancer agents.\textsuperscript{11-16} Another important aspect, especially from the catalytic perspective involves the design of Ru=O functional groups and analogues capable of reversibly accepting multiple electrons and protons within the relative potential range.\textsuperscript{19-21} The capacity to modify their environment in order to induce electronic as well as steric effects will allow fabricating tailored catalysis for specific reactions. Inclusion of the pyridazine ring in the backbone of \( hpzp \) ligand results in a more pronounced partitioning of the ligand into distinct bidentate domains than is the case with linear polypyridines. This facilitates the formation of mononuclear and binuclear systems. The former has the potential to behave as metallo-ligands in the development of homo/hetero bimetallic systems.\textsuperscript{22-25}

In the present chapter, we have synthesized new nitrogen based ligands such as 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (\textit{pp-Cl}) and 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (\textit{bppp}) (Chart 5.1) which easily form mono and binuclear complexes with arene ruthenium, Cp* rhodium and Cp* iridium complexes (Cp* = \( \eta^5 \)-C\(_5\)Me\(_5\)). All these new complexes were characterized by elemental analyses, IR, \(^1\)H-NMR, UV-Visible and mass spectrometry as well as X-crystallographic analyses for some representative complexes.

![Chart 5.1: Ligands used in this study](image)

3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (\textit{pp-Cl})
3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (\textit{bppp})
5.2 Experimental

5.2.1 Preparations of ligands: pp-Cl and bppp

A mixture of 3,6-dichloropyridazine (500 mg, 3.35 mmol), 3-(2-pyridyl)-1H-pyrazole \(^{31}\) (1 g, 6.88 mmol), potassium carbonate (1.05 g, 7.59 mmol) and tetrabutylammonium bromide (1.2 g) in 10 ml of acetone was dissolved. It was stirred and refluxed for forty hours and cooled to room temperature. Then the reaction mixture was poured into 100 ml of water, resulted a whitish precipitate; it was filtered off, washed with excess water and air dried. It was purified by chromatography on silica gel using chloroform as the eluent to give the analytically pure ligand 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (pp-Cl) (20%) as a pale yellow color powder and the second fraction was eluted with chloroform/methanol (10:1) give the analytically pure ligand 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (bppp) (80%) as a colorless solid.

5.2.1.1 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (pp-Cl)

Pale yellow solid, yield 120 mg (13%): \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 8.77 (d, 1H, \(^3J = 2.80\) Hz, Ha), 8.68 (d, 1H, \(3J = 4.40\) Hz, Hf), 8.34 (d, 1H, \(3J = 9.20\) Hz, Hg), 8.04 (d, 1H, \(3J = 8.00\) Hz, Hh), 7.77 (dt, 1H, \(3J = 1.60\) Hz, Hd), 7.63 (d, 1H, \(3J = 9.20\) Hz, Hc), 7.28 (dt, 1H, \(3J = 1.60\) Hz, Hb), 7.18 (d, 1H, \(3J = 2.40\) Hz, He); ESI-MS (m/z): 258.1 (100%) [M+1]; UV–Vis (acetonitrile, \(\lambda_{\text{max}}\) nm (\(\varepsilon10^{-5}\)M\(^{-1}\) cm\(^{-1}\))): 318 (0.37); Anal. Calc. For C\(_{12}\)H\(_8\)ClN\(_5\) (257.6): C, 55.93; H, 3.13; N, 27.18; Found: C, 54.88; H, 3.15; N, 27.02%.

5.2.1.2 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (bppp)

White solid, yield 780 mg (63%): \(^1\)H NMR (400 MHz, CDCl\(_3\), \(\delta\)): 8.81 (d, 2H, \(^3J = 2.40\) Hz, Haa'), 8.71 (d, 2H, \(^3J = 4.40\) Hz, Hff'), 8.52 (s, 2H, Hgg'), 8.11 (d, 2H, \(^3J = 8.00\), Hdd'), 7.80 (dt, 2H, \(^3J = 1.60\) Hz, Hcc'), 7.29 (dt, 2H, \(^3J = 1.60\) Hz, Hbb'), 7.21 (d, 2H, \(^3J = 2.80\) Hz, Hee'); ESI-MS (m/z): 367.2 (100%) [M+1]; UV–Vis (acetonitrile, \(\lambda_{\text{max}}\) nm (\(\varepsilon10^{-5}\)M\(^{-1}\) cm\(^{-1}\))): 316 (0.41), 331 (0.33); Anal. Calc. For C\(_{20}\)H\(_{14}\)N\(_8\) (366.3): C, 65.56; H, 3.85; N, 30.58; Found: C, 65.38; H, 3.89; N, 30.46%

5.2.1.3 4,6-bis(3-pyridyl-1-pyrazolyl)pyrimidine (bppm)

The of bppm ligand was synthesized and isolated in a similar manner described for the synthesis of bppp taking 500 mg (3.35 mmol) of 4,6-dichloropyrimidine, 3-(2-pyridyl)-
1H-pyrazole (1 g, 6.88 mmol), potassium carbonate (1.05 g, 7.59 mmol) and tetrabutylammonium bromide (1.2 g) in 10 ml of acetone was dissolved. White solid, yield 780 mg (63%): 1H NMR (400 MHz, CDCl₃, δ): 8.85 (d, 2H, J = 2.40 Hz), 8.73 (s, 1H), 8.70 (d, 2H, J = 1.60 Hz), 8.66 (s, 1H), 8.28 (d, 2H, J = 7.20), 7.86 – 7.82 (dt, 2H, J = 1.60 Hz), 7.34 – 7.31 (dt, 2H, J = 1.60 Hz), 7.22 (d, 2H, J = 2.80 Hz); ESI-MS (m/z): 367.2 (100%) [M+1]; UV-Vis (acetonitrile, λmax nm (ε10⁻⁵ M⁻¹ cm⁻¹)): 318 (0.41), 332 (0.33); Anal. Calc. For C₂₀H₁₄N₈ (366.3): C, 65.56; H, 3.85; N, 30.58; Found: C, 65.38; H, 3.89; N, 30.46%

5.2.2 General procedure for the preparation of the mononuclear complexes 1 and 2

A mixture of [(η⁶-arene)Ru(u-Cl)Cl₂ (arene = C₆H₆ and p-iPrC₆H₄Me) (0.07 mmol), ligand pp-Cl (0.18 mmol) and 2.5 equivalents of ~PF₆ in dry methanol (15 ml) was stirred at room temperature for 6 hours. The precipitate was separated by filtration, washed with cold methanol and diethyl ether to remove excess ligand and dried in vacuo.

5.2.2.1 [(η⁶-C₆H₆)Ru(pp-Cl)Cl]PF₆ ([1]PF₆)
Orange-yellow solid, yield 75 mg (87%), 1H NMR (400 MHz, CD₃CN, δ): 9.55 (d, 1H, J = 5.60 Hz ), 8.97 (d, 1H, J = 2.80 Hz), 8.72 (d, 1H, J = 7.28 Hz), 8.45 (m, 2H), 8.32 (t, 1H, J = 7.60 Hz, 7.60 Hz), 7.78 (m, 2H), 5.95 (s, 6H); IR (KBr, cm⁻¹): ν(P-F) 844s; 1604m, 1408m, 558m; ESI-MS (m/z): 472.1 (100%) [M-PF₆⁺]; UV-Vis (acetonitrile, λmax nm (ε10⁻⁵ M⁻¹ cm⁻¹)): 310 (0.19); Anal. Calc. For C₁₈H₁₄Cl₂N₃RuPF₆ (617.2): C, 35.02; H, 2.29; N, 11.35; Found: C, 34.88; H, 2.35; N, 11.28%.

5.2.2.2 [(η⁶-p-iPrC₆H₄Me)Ru(pp-Cl)Cl]PF₆ ([2]PF₆)
Dark orange solid, yield 83 mg (90%), 1H NMR (400 MHz, CD₃CN, δ): 9.22 (d, 1H, J = 5.60 Hz ), 8.75 (d, 1H, J = 4.80 Hz), 8.62 (d, 1H, J = 3.20 Hz), 8.19 – 8.12 (m, 3H), 7.66 (dd, 1H, J = 7.60 Hz, 7.60 Hz), 7.40 (d, 1H, J = 3.2 Hz) 5.72 (d, 1H, J = 6.40 Hz, Arp-cy), 5.46 (d, 1H, J = 6.00 Hz, Arp-cy), 5.30 (d, 1H, J = 6.00 Hz, Arp-cy), 5.18 (d, 1H, J = 6.00 Hz, Arp-cy), 2.37 (sept, 1H, CH(CH₃)₂), 2.17 (s, 3H, Arp-cy-Me), 1.21 (d, 3H, CH(CH₃)₂), 1.18 (d, 3H, CH(CH₃)₂); IR (KBr, cm⁻¹): ν(P-F) 844s; 1629m, 1406m, 763m, 558m; ESI-MS (m/z): 527.2 (100%) [M-PF₆⁺]; UV-Vis (acetonitrile, λmax nm (ε10⁻⁵ M⁻¹ cm⁻¹)): 309 (0.28); Anal. Calc. For C₂₂H₂₂Cl₂N₃RuPF₆ (673.3): C, 39.24; H, 3.29; N, 10.40; Found: C, 39.11; H, 3.35; N, 10.31%.
5.2.3 General procedure for the preparation of the mononuclear complexes 3 and 4
A mixture of \([\eta^5-C_5Me_5]M(\mu-Cl)Cl\)\(_2\) (M = Rh, Ir) (0.07 mmol), ligand \(pp-Cl\) (0.15 mmol) and 2.5 equivalents of ammonium hexafluorophosphate in dry methanol (15 ml) was refluxed for 4 hours. The reaction mixture was cooled over night at room temperature during this time dark yellow color crystalline compound formed. It was separated by filtration, washed with cold methanol and diethyl ether to remove excess ligand and dried in vacuo.

5.2.3.1 \([\eta^5-C_5Me_5]Rh(pp-Cl)Cl\)PF\(_6\) ([3]PF\(_6\))
Dark yellow in color, yield 86 mg (91%), \(^1\)H NMR (400 MHz, CD\(_3\)CN, \(\delta\)): 8.91 (d, 1H, \(^3J = 5.20\) Hz), 8.67 (d, 1H, \(^3J = 4.40\) Hz), 8.50 (d, 1H, \(^3J = 7.60\) Hz), 8.36 (m, 3H), 7.44 (dt, 1H, \(^3J = 5.20\) Hz, 6.80 Hz), 7.22 (d, 1H, \(^3J = 2.4\) Hz), 2.15 (s, 15H, C\(_5\)Me\(_5\)); IR (KBr, cm\(^{-1}\)): \(\nu(P-F)\) 845s; 1626m, 1458m, 759m, 558m; ESI-MS (m/z): 531.3 (100%) \([M-PF_6]^+\); UV–Vis \{acetonitrile, \(\lambda_{\text{max}}\) nm \((\varepsilon 10^{-5}\text{M}^{-1}\text{cm}^{-1})\): 316 (0.27); Anal. Calc. For C\(_{22}\)H\(_{23}\)Cl\(_2\)N\(_3\)RhPF\(_6\) (676.3): C, 39.07; H, 3.43; N, 10.49; Found: C, 39.01; H, 3.45; N, 10.33%.

5.2.3.2 \([\eta^5-C_5Me_5]Ir(pp-Cl)Cl\)PF\(_6\) ([4]PF\(_6\))
Dark yellow color, yield 89 mg (88%), \(^1\)H NMR (400 MHz, CD\(_3\)CN, \(\delta\)): 9.01 (d, 1H, \(^3J = 5.60\) Hz), 8.71 (d, 1H, \(^3J = 2.32\) Hz, 5.60 Hz), 8.35 (m, 3H), 7.35 (d, 1H, \(^3J = 4.80\) Hz), 1.88 (s, 15H, C\(_5\)Me\(_5\)); IR (KBr, cm\(^{-1}\)): \(\nu(P-F)\) 845s; 1631m, 1495m, 760m, 558m; ESI-MS (m/z): 620.9 (100%) \([M-PF_6]^+\); UV–Vis \{acetonitrile, \(\lambda_{\text{max}}\) nm \((\varepsilon 10^{-5}\text{M}^{-1}\text{cm}^{-1})\): 318 (0.29); Anal. Calc. For C\(_{22}\)H\(_{23}\)Cl\(_2\)N\(_3\)IrPF\(_6\) (765.4): C, 34.52; H, 3.03; N, 9.05; Found: C, 34.25; H, 3.05; N, 9.00%.

5.2.4 General procedure for the preparation of the mononuclear complexes 5 and 6
A mixture of \([\eta^6\text{-arene}]Ru(\mu-Cl)Cl\)\(_2\) (arene = C\(_6\)H\(_6\) and \(p^\prime\)-PrC\(_6\)H\(_4\)Me) (0.07 mmol), ligand \(hppp\) (0.15 mmol) and 2.5 equivalents of ammonium hexafluorophosphate in dry methanol (15 ml) was stirred at room temperature for 6 hours. The precipitate was separated by filtration, washed with cold methanol and diethyl ether to remove excess ligand and dried in vacuo.
5.2.4.1 [(η⁶-C₆H₆)Ru(bppp)Cl]PF₆ ([5]PF₆)

Brown color; Yield 85 mg (84%), ¹H NMR (400 MHz, CD₃CN, δ): 9.48 (d, 1H, ³J = 5.20 Hz), 8.68 (d, 1H, ³J = 5.64 Hz), 8.62 (d, 1H, ³J = 3.20 Hz), 8.32 – 8.28 (m, 5H), 7.76 (dt, 2H), 7.62 (t, 1H, ³J = 3.32 Hz), 7.43 (d, 1H, ³J = 3.24 Hz), 7.26 (d, 1H, ³J = 4.20 Hz), 7.20 (d, 1H, ³J = 4.00 Hz), 6.01 (s, 6H, C₆H₆); IR (cm⁻¹): 1614m, 1454s, 1437s, 844s, 788s, 558m; ESI-MS: 580.9 [M⁺], 545.2 [M - Cl]; UV-Vis {acetonitrile, λₘₐₓ nm (ε₁₀⁻⁵ M⁻¹ cm⁻¹)}: 276 (0.57), 314 (0.92), 417 (0.04); Anal. Calc. for C₂₆H₁₉ClNsRuPF₆ (725.9): C, 43.01; H, 2.78; N, 15.43. Found: C, 42.89; H, 2.87; N, 15.28%.

5.2.4.2 [(η⁶-p-PrC₆H₅Me)Ru(bppp)Cl]PF₆ ([6]PF₆)

Orange-yellow solid, Yield 89 mg (83%), ¹H NMR (400 MHz, CD₃CN, δ): 9.55 (d, 1H, ³J = 5.20 Hz), 8.72 (d, 1H, ³J = 5.64 Hz), 8.68 (d, 1H, ³J = 3.20 Hz), 8.20 – 8.18 (m, 4H), 7.68 (dt, 2H), 7.42 (t, 1H, ³J = 3.32 Hz), 7.38 (d, 1H, ³J = 4.80 Hz), 7.22 (d, 1H, ³J = 4.20 Hz), 7.18 (d, 2H, ³J = 5.60 Hz), 5.72 (d, 1H, ³J = 6.40 Hz, Arp-cy), 5.42 (d, 1H, ³J = 6.00 Hz, Arp-cy), 5.39 (d, 1H, ³J = 6.00 Hz, Arp-cy), 5.29 (d, 1H, ³J = 6.00 Hz, Arp-cy), 2.70 (sept, 1H, CH(CH₃)₂), 2.33 (s, 3H, Arp-cy-Me), 1.71 (d, 3H, ³J = 6.20 Hz, CH(CH₃)₂), 1.69 (d, 3H, ³J = 6.80 Hz, CH(CH₃)₂); IR (cm⁻¹): 1604m, 1449m, 1437m, 843s, 783m, 558m; ESI-MS: 637.1 [M⁺], 602.1 [M - Cl]; UV-Vis {acetonitrile, λₘₐₓ nm (ε₁₀⁻⁵ M⁻¹ cm⁻¹)}: 274 (0.57), 313 (0.89), 418 (0.05); Anal. Calc. for C₃₀H₂₅ClNsRuPF₆ (782.1): C, 46.07; H, 3.61; N, 14.33. Found: C, 45.97; H, 3.68; N, 14.17%.

5.2.5 General procedure for the preparation of the mononuclear complexes 7 and 8

A mixture of [(η⁶-C₅Me₅)M(u-Cl)Cl]₂ (M = Rh, Ir) (0.07 mmol), ligand bppp (0.15 mmol) and 2.5 equivalents of ammonium hexafluorophosphate in dry methanol (15 ml) was refluxed for 4 hours. The reaction mixture was cooled over night at room temperature during this time dark yellow color crystalline compound formed. It was separated by filtration, washed with cold methanol and diethyl ether to remove excess ligand and dried under vacuum.

5.2.5.1 [(η⁶-C₅Me₅)Rh(bppp)Cl]PF₆ ([7]PF₆)

Dark yellow color, yield 96 mg (84%), ¹H NMR (400 MHz, CD₃CN, δ): 9.39 (d, 1H, ³J = 5.20 Hz), 8.68 (d, 1H, ³J = 5.40 Hz), 8.54 (d, 1H, ³J = 3.64 Hz), 8.18 - 8.10 (m, 4H), 7.61 (dt, 2H), 7.48 (d, 1H, ³J = 3.60 Hz), 7.32 (d, 1H, ³J = 4.8 Hz), 7.22 (d, 1H, ³J = 4.20 Hz), 7.16 (d, 2H, ³J = 3.64 Hz), 2.11 (s, 15H, C₅Me₅); ESI-MS (m/z): 639.2 (100%) [M-PF₆⁺];
IR (KBr, cm\(^{-1}\)): \(\nu(P-F)\) 845 s; 1626 m, 1458 m, 759 m, 558 m; UV–Vis (acetonitrile, \(\lambda_{\text{max}}\) nm (\(\varepsilon 10^3\text{M}^{-1}\text{cm}^{-1}\))): 276 (0.57), 315 (0.87), 419 (0.04); Anal. Calc. For C\(_{30}\)H\(_{29}\)ClN\(_8\)RhPF\(_6\) (784.93): C, 45.91; H, 3.72; N, 14.28; Found: C, 45.93; H, 3.77; N, 14.30%.

5.2.5.2 \([\eta^5-C_5Me_5]Ir(bppp)Cl\)PF\(_6\) ([8]PF\(_6\))

Dark yellow in color, yield 95 mg (83%): \(^1\text{H}\) NMR (400 MHz, CD\(_3\)CN, \(\delta\)): 9.40 (d, 1H, \(\nu 3 J = 5.32\) Hz), 8.72 (d, 1H, \(\nu 3 J = 5.40\) Hz), 8.62 (d, 1H, \(\nu 3 J = 3.64\) Hz ), 8.20 – 8.14 (m, 4H), 7.65 (dt, 2H), 7.48 (d, 1H, \(\nu 3 J = 3.60\) Hz), 7.31 (d, 1H, \(\nu 3 J = 4.8\) Hz), 7.18 (d, 1H, \(\nu 3 J = 4.80\) Hz), 7.15 (d, 2H, \(\nu 3 J = 3.60\) Hz), 1.98 (s, 15H, C\(_5\) Me\(_5\) ); IR (cm\(^{-1}\)): 1614 m, 1454 m, 1437 m, 844 s, 788 m, 558 m; ESI-MS: 729.2 (100%) [M–PF\(_6\)]\(^+\); IR (KBr, cm\(^{-1}\)): \(\nu(P-F)\) 845 s; 1631 m, 1495 m, 760 m, 558 m; UV–Vis (acetonitrile, \(\lambda_{\text{max}}\) nm (\(\varepsilon 10^3\text{M}^{-1}\text{cm}^{-1}\))): 277 (0.58), 314 (0.95), 423 (0.04); Anal. Calc. For C\(_{30}\)H\(_{29}\)ClN\(_8\)IrPF\(_6\) (874.24): C, 41.22; H, 3.34; N, 12.82; Found: C, 41.19; H, 3.38; N, 12.73%.

5.2.6 General procedure for the syntheses of the dinuclear complexes 9 and 10

A mixture of \([\eta^5\text{-arene}]Ru(\mu-Cl)Cl\)\(_2\) (arene = C\(_6\)H\(_6\) and \(p\)-PrC\(_6\)H\(_4\)Me) (0.10 mmol) and bppp (0.10 mmol) was suspended in methanol (20 ml) and stirred at room temperature for 6 hours. Then, ammonium hexafluorophosphate (46 mg, 0.25 mmol) was added to the reaction mixture and further stirred for 3 hours. The precipitate was filtered, washed with methanol and diethylether (3 X 10 ml) and dried in vacuo.

5.2.6.1 \([\eta^5\text{-C}_6\text{H}_6\text{Cl}]\text{RuCl}_2(\mu\text{-bppp})\)PF\(_6\) ([9]PF\(_6\)\(_2\))

Orange-yellow solid, Yield 91 mg (85%): \(^1\text{H}\) NMR (400 MHz, CD\(_3\)CN, \(\delta\)): 9.34 (d, 2H, \(\nu 3 J = 4.20\) Hz), 9.14 (s, 2H), 8.81 (d, 2H, \(\nu 3 J = 2.40\) Hz ), 8.24 (d, 2H, \(\nu 3 J = 6.80\) Hz), 7.72 (t, 2H, \(\nu 3 J = 5.60\), 4.80 Hz), 7.50 (d, 2H, \(\nu 3 J = 2.40\) Hz), 7.36 (d, 2H, \(\nu 3 J = 4.80\) Hz), 5.75 (s, 12H, C\(_6\)H\(_6\) ); IR (cm\(^{-1}\)): 1614m, 1454m, 1437m, 844s, 788m, 558m; ESI-MS: 940.6[M\(^{2+}\)PF\(_6\)]\(^+\); UV–Vis (acetonitrile, \(\lambda_{\text{max}}\) nm (\(\varepsilon 10^3\text{M}^{-1}\text{cm}^{-1}\))): 277 (0.58), 314 (0.95), 423 (0.04); Anal. Calc. for C\(_{32}\)H\(_{26}\)NsCl\(_2\)RuP\(_2\)F\(_{12}\) (1085.6): C, 35.40; H, 2.41; N 10.32. Found: C, 35.33; H, 2.47; N, 10.18%.

5.2.6.2 \([\eta^5\text{-p-PrC}_6\text{H}_4\text{Me}]\text{RuCl}_2(\mu\text{-bppp})\)PF\(_6\) ([10]PF\(_6\)\(_2\))

Orange-yellow solid, Yield 99 mg (84%): \(^1\text{H}\) NMR (400 MHz, CD\(_3\)CN, \(\delta\)): 9.55 (d, 2H, \(\nu 3 J = 5.60\) Hz), 9.37 (s, 2H), 9.14 (d, 2H, \(\nu 3 J = 2.80\) Hz ), 8.52 (d, 2H, \(\nu 3 J = 7.60\) Hz), 8.48 (t, 2H, \(\nu 3 J = 7.20\), 7.60 Hz), 8.36 (t, 2H), 7.86 (d, 2H, \(\nu 3 J = 2.40\) Hz), 6.10 (d, 2H, \(\nu 3 J = 6.00\) Hz), 2.86 (d, 2H, \(\nu 3 J = 1.80\) Hz), 2.78 (s, 6H, C\(_3\)H\(_6\) ); IR (KBr, cm\(^{-1}\)): 1614 m, 1454 m, 1437 m, 1403 m, 844 m, 788 m, 558 m; ESI-MS: 940.6[M\(^{2+}\)PF\(_6\)]\(^+\); UV–Vis (acetonitrile, \(\lambda_{\text{max}}\) nm (\(\varepsilon 10^3\text{M}^{-1}\text{cm}^{-1}\))): 284 (0.61), 317 (0.95), 429 (0.04); Anal. Calc. for C\(_{32}\)H\(_{26}\)NsCl\(_2\)RuP\(_2\)F\(_{12}\) (1085.6): C, 35.40; H, 2.41; N 10.32. Found: C, 35.33; H, 2.47; N, 10.18%.
5.2.7 General procedure for the syntheses of the dinuclear complexes 11 and 12

A mixture of \([(\eta^5-C_5Me_5)M(\mu-Cl)Cl]_2\) (M = Rh and Ir) (0.10 mmol) and bppp (0.10 mmol) was suspended in methanol (20 ml) and refluxed for 5 hours. Then, ammonium hexafluorophosphate (23 mg, 0.13 mmol) was added to the reaction mixture and further refluxed for an hour. During this time was precipitate was observed. The precipitate was filtered, washed with methanol and diethylether (3 X 10 ml) and dried in vacuo.

5.2.7.1 \([(\eta^5-C_5Me_5)RhCl]_2(\mu-bppp)(PF_6)_2\) (11) (PF_6)_2

Dark yellow color, yield 101 mg (84%): ^1H NMR (400 MHz, CD_3CN, δ): 9.38 (d, 2H, J = 5.40 Hz), 9.17 (s, 2H), 8.81 (d, 2H, J = 2.32 Hz ), 8.24 (d, 2H, J = 6.80 Hz), 7.75 (t, 2H, J = 5.20, 4.80 Hz), 7.52 (d, 2H, J = 2.32 Hz), 7.37 (d, 2H, J = 4.32 Hz), 2.05 (s, 30H, C_5Mes); IR (cm⁻¹): 1604m, 1449m, 1437m, 843s, 783m, 558m; ESI-MS: 1058.6 [M^2+PF_6]^+; UV-Vis (acetonitrile, \(\lambda_{\text{max}}\) nm (e10^5 M⁻¹ cm⁻¹)): 276 (0.39), 314 (0.67), 420 (0.04); Anal. Calc. for C_{40}H_{42}N_8ChRhP_2F_{12} (1203.5): C, 39.92; H, 3.69; N, 9.31. Found: C, 39.21; H, 3.72; N, 9.27%.

5.2.7.2 \([(\eta^5-C_5Me_5)IrCl]_2(\mu-bppp)(PF_6)_2\) (12) (PF_6)_2

Dark yellow color, yield 105 mg (86%): ^1H NMR (400 MHz, CD_3CN, δ): 9.31 (d, 2H, J = 4.36 Hz), 9.14 (s, 2H), 8.78 (d, 2H, J = 2.80 Hz ), 8.21 (d, 2H, J = 6.32 Hz), 7.72 (t, 2H, J = 5.60, 4.80 Hz), 7.50 (d, 2H, J = 2.40 Hz), 7.36 (d, 2H, J = 4.80 Hz), 1.99 (s, 15H, C_5Mes); IR (cm⁻¹): 1604m, 1449m, 1437m, 843s, 783m, 558m; ESI-MS: 1236.2 [M^2+PF_6]^+; UV-Vis (acetonitrile, \(\lambda_{\text{max}}\) nm (e10^5 M⁻¹ cm⁻¹)): 273 (0.46), 313 (0.71), 418 (0.04); Anal. Calc. for C_{40}H_{42}N_8Cl_2IrP_2F_{12} (1382.1): C, 34.76; H, 3.21; N, 8.11. Found: C, 34.61; H, 3.25; N, 8.01%.
5.2.8 Single crystal X-ray structure analyses

X-ray quality crystals of complexes 2 and 7 were grown by slow diffusion of hexane in dichloromethane / acetonitrile solution of corresponding complexes. The X-ray intensity data were measured at 293(2)° K on a Bruker Apex II CCD area detector employing graphite monochromated using Mo-Kα radiation (λ = 0.71073 Å). An empirical absorption correction was made by modeling a transmission surface by spherical harmonics employing equivalent reflections with l>2σ(l) using the program SADBAD. The structures were solved by direct methods using the program SHELXS 97 and refined by full matrix least squares base on F^2 using the program SHELXL-97. The weighting scheme used was \( W = 1/[\sigma^2(F_{o2}) + 0.0311P^2 + 3.5016P] \) where \( P = (F_{o2}^2 + 2F_{c2}^2)/3 \).

Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a “riding” model. Refinement converged at a final R = 0.0423 and 0.0454 (for complexes 2 and 7 respectively, for observed data F^2), and wR^2 = 0.0804 and 0.0667 (for complexes 2 and 7 respectively, for unique data F^2). Regarding complex 7 molecular structure, we encountered two difficulties, they are (i) one is assigning N(8) and C(17), and another one is (ii) occupancy of the solvent molecule acetonitrile. The matter regarding an ambiguity in assigning N(8) and C(17), exchanging the atoms did not improve the refinement. So the labelling was done in analogy with other compounds and represents the most probable orientation of the molecular fragment. The second factor is now explained on the following lines: the central atom of solvent molecule with occupancy of C is 0.5. Since the solvent molecule is acetonitrile, the two heavy peripheral atoms are N and C. It appears that we cannot differentiate between N and C, which can be due to the random orientation of N and C (they exchange the sites). We also could not locate the H atoms associated with the peripheral C atom. This peripheral site was treated as a 50/50 mixture of C and N, which considering the occupancy of this site yields one molecule of acetonitrile (per two molecules of the complex). The distance between the central C atom and peripheral atoms is 1.55 Å. While other solvent molecules may be present, only acetonitrile molecule has been located from the residual density map. Its presence was manifested by a large residual density, and its introduction lowered the R value from 5.55 to 4.43%. Details of crystallographic data collection parameters and refinement are summarized in table 5.1. Selected bond lengths and angles are tabulated in table 5.2.
5.3 Results and discussion

5.3.1 Synthesis of ligands

The ligands 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine ($pp$-$Cl$) and 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine were synthesized by the condensation of 3,6-dichloropyridazine and 3-(2-pyridyl)-1H-pyrazole. The reaction was carried out in acetone under refluxing condition in the presence of potassium carbonate and the phase transfer catalyst tetrabutylammonium bromide. The resulting compounds were characterized by spectroscopic methods as detailed in the experimental section.

5.3.2 Synthesis of the mononuclear complexes 1 to 8 as a hexafluorophosphate salts

The mononuclear cationic arene ruthenium and pentamethylcyclopentadienyl rhodium and iridium complexes having 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine ($pp$-$Cl$) and 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine ($bppp$) ligands viz., \([\eta^6-\text{C}_8\text{H}_8]\text{RuCl}(pp-Cl)]PF_6 \[1\]PF_6, \([\eta^6-p-\text{PrC}_6\text{H}_4\text{Me}]\text{RuCl}(pp-Cl)]PF_6 \[2\]PF_6, \([\eta^5-\text{C}_5\text{Me}_5]\text{RhCl}(pp-Cl)]PF_6 \[3\]PF_6 and \([\eta^5-\text{C}_5\text{Me}_5]\text{IrCl}(pp-Cl)]PF_6 \[4\]PF_6 (Scheme 5.1) and \([\eta^6-\text{C}_8\text{H}_8]\text{RuCl}(bppp)]PF_6 \[5\]PF_6, \([\eta^6-p-\text{PrC}_6\text{H}_4\text{Me}]\text{RuCl}(bppp)]PF_6 \[6\]PF_6, \([\eta^5-\text{C}_5\text{Me}_5]\text{RhCl}(bppp)]PF_6 \[7\]PF_6 and \([\eta^5-\text{C}_5\text{Me}_5]\text{IrCl}(bppp)]PF_6 \[8\]PF_6 (Scheme 5.2) have been prepared by the reaction of arene or pentamethylcyclopentadienyl complexes \([\eta^6-\text{arene}]\text{Ru}($\mu$-Cl)Cl]_2 \text{(arene} = \text{C}_8\text{H}_8 \text{and} \text{p-PrC}_6\text{H}_4\text{Me}) \text{and} \([\eta^5-\text{C}_5\text{Me}_5]M($\mu$-Cl)Cl]_2 \text{(}M = \text{Rh \text{and} Ir) \text{with 2.1}} \text{equivalents of ligand 3-chloro-6-(1-pyridyl-3-pyrazolyl)pyridazine (}pp\text{-Cl}) \text{or 3,6-bis(1-pyridyl-3-pyrazolyl)-pyridazine (}bppp\text{) in methanol. The complexes 1 to 8 were isolated as hexafluorophosphate salts and exhibit an orange-red color. They are non-hygroscopic, air-stable, shiny crystalline solids sparingly soluble in methanol, dichloromethane and chloroform, but soluble in acetone and acetonitrile. All these metal complexes were fully characterized by IR, NMR and UV-Vis and mass spectrometry.
The infrared spectra of the complexes 1 to 8 exhibit a strong band in the region 844-850 cm\(^{-1}\), a typical \(v_{P-F}\) stretching band and for the PF\(_6\) anions as well as peaks
corresponding to phenyl, pyridyl, pyrazolyl and pyridazine (C=C and C=N) rings were observed.

The mass spectra of these compounds exhibited the corresponding molecular ion peaks m/z at 472, 527, 531, 621, 581, 637, 639 and 729. For example the mass spectrum of the complex 2 is depicted in figure 5.1.

![Mass spectrum of complex 2](image)

**Figure 5.1: Mass spectrum of the complex \( ([\eta^6-p-iPrC_6H_4Me]Ru(pp-Cl)Cl)PF_6 ([2]PF_6) \)**

The \(^1\)H NMR spectrum of free ligands 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (pp-Cl) exhibit a characteristic set of eight resonances at 8.77 (d, 1H), 8.68 (d, 1H), 8.34 (d, pyrazolyl, pyridazine and pyridyl ring protons of the 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (bppp) ligand, indicating formation of mononuclear complexes. Besides these resonances complex 1 and 5 exhibit a singlet at \( \delta = 5.95 \) and 5.92 respectively for the protons of the benzene ligand. Complexes 2 and 6 exhibits two doublets at \( \delta = 1.71 - 1.69 \), as well as a septet at \( \delta = 2.70 - 2.32 \) for the protons of the isopropyl group and a singlet at 2.17 ppm for the methyl protons of p-cymene ring. The four doublets observed at 5.59 - 5.39 correspond to the aromatic p-cymene ring CH protons. This unusual pattern is due to the diastereotopic methyl protons of the isopropyl group and aromatic protons of the p-cymene ligand, since the ruthenium atom is stereogenic due to the coordination of four different ligand atoms and chiral nature of
metal atom.\textsuperscript{26-28} Interestingly the chemical shifts of complex 6 shown down field compared to complex 2 of p-cymene ligand. Complexes 3, 4, 7 and 8 exhibit a strong peak at $\delta = 2.15$, 1.88, 2.11 and 1.98 for pentamethylcyclopentadienyl ligand respectively, which are slightly shifted downfield in comparison to the starting complexes.

5.3.3 Crystal structure analysis of \[(\eta^6-p^1\text{PrC}_6\text{H}_4\text{Me})\text{Ru(}pp\text{-Cl})\text{Cl}]PF_6 ([2]PF_6)\) and \[(\eta^5-C_5\text{Me}_5)\text{Rh(bppp)}\text{Cl}]PF_6 ([7]PF_6)\)

The molecular structure of \[(\eta^6-p^1\text{PrC}_6\text{H}_4\text{Me})\text{Ru(}pp\text{-Cl})\text{Cl}]PF_6 ([2]PF_6)\) and \[(\eta^5-C_5\text{Me}_5)\text{Rh(bppp)}\text{Cl}]PF_6 ([7]PF_6)\) have been established by single-crystal X-ray structure analysis. Both complexes shown a typical piano-stool geometry with the metal centre coordinated by the aromatic ligand, chloride and a chelating N,N'-ligand (see figures 5.2 and 5.3). The metal atom is in octahedral arrangement and the \textit{pp-Cl} or \textit{bppp} ligand is found to coordinate through the N1 atom of the pyridine moiety and the N2 atom of the pyrazolyl ring to generate a five-membered ring metallo-cycle (see Figures 5.2 and 5.3). In these complexes, the N atom of pyridazine points away from the metal centre and show no interaction with neighboring cations. Selected bond lengths and angles for complexes 2 and 7 are presented in Table 5.2.

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<tr>
<td>Chemical formula</td>
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<td>C₃₀H₂₉ClF₄N₃PRh.0.5CH₃CN</td>
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<tr>
<td>Crystal system</td>
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<td>Monoclinic</td>
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<tr>
<td>Formula weight</td>
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<td>803.96</td>
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<tr>
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<td>Space group</td>
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<td>Crystal color and shape</td>
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<td>Plate, yellow</td>
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<tr>
<td>Crystal size (mm)</td>
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<td>0.22 × 0.14 × 0.12</td>
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<tr>
<td>a (Å)</td>
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<td>8.5156 (17)</td>
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<tr>
<td>b (Å)</td>
<td>22.7250 (16)</td>
<td>19.095 (4)</td>
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<tr>
<td>c (Å)</td>
<td>22.133 (2)</td>
<td>22.334 (5)</td>
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<tr>
<td>α (°)</td>
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<td>-</td>
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<tr>
<td>β (°)</td>
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<td>90.46 (3)</td>
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<tr>
<td>γ (°)</td>
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<td>-</td>
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<tr>
<td>V (Å³)</td>
<td>5073.2 (7)</td>
<td>3631.5 (13)</td>
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<tr>
<td>Z</td>
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<td>4</td>
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<tr>
<td>T (K)</td>
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<tr>
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<td>μ (mm⁻¹)</td>
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<td>Scan range (°)</td>
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<td>2.11°&lt; θ &lt;20.00</td>
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<td>Unique reflections</td>
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<td>Rₓ</td>
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<td>Final R indices [I&gt;2σ(I)]</td>
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<td>R indices (all data)</td>
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<td>Max, Min Δρ (e Å⁻³)</td>
<td>0.696, -0.718</td>
<td>0.284, -0.261</td>
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Table 5.2: Selected bond lengths (Å) and angles (°) for compounds [1]PF₆ and [7]PF₆.

<table>
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<tr>
<td><strong>Interatomic distances</strong></td>
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<tr>
<td>Ru-N1</td>
<td>2.099(3)</td>
<td>2.080(1)</td>
</tr>
<tr>
<td>Ru-N2</td>
<td>2.089(3)</td>
<td>2.160(5)</td>
</tr>
<tr>
<td>Ru-Cl1</td>
<td>2.406(2)</td>
<td>2.396(4)</td>
</tr>
<tr>
<td>Ru-centroid (C₆ ring)</td>
<td>1.683</td>
<td>Rh-centroid (C₅ ring) 1.79</td>
</tr>
<tr>
<td>C5-C6</td>
<td>1.351(5)</td>
<td>C5-C6</td>
</tr>
<tr>
<td>N1-C1</td>
<td>1.390(5)</td>
<td>N1-C1</td>
</tr>
<tr>
<td>N2-N3</td>
<td>1.420(5)</td>
<td>N2-N3</td>
</tr>
<tr>
<td><strong>Angles</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1-Ru-N2</td>
<td>75.50(1)</td>
<td>N1-Rh-N2</td>
</tr>
<tr>
<td>N1-Ru-Cl1</td>
<td>83.80(1)</td>
<td>N1-Rh-Cl1</td>
</tr>
<tr>
<td>N2-Ru-Cl1</td>
<td>84.52(1)</td>
<td>N2-Rh-Cl1</td>
</tr>
<tr>
<td>Ru1-N1-C5</td>
<td>116.90(2)</td>
<td>Rh1-N1-C5</td>
</tr>
<tr>
<td>Ru1-N2-C6</td>
<td>115.50(2)</td>
<td>Rh1-N2-C6</td>
</tr>
</tbody>
</table>

Figure 5.2: Molecular structure of complex $[$(η⁵-p-JPrC₆H₄Me)Ru(pp-Cl)Cl]$PF₆$ ([2]PF₆).
In the mononuclear complex 2 the N1-metal [2.099(3) Å] distance of the pyridyl ring is slightly longer than the corresponding pyrazolyl, N2-metal distance [2.089(3) Å], in contrast for complex 7 the N1-metal [2.082(1) Å] distance slightly shorter than the corresponding pyrazolyl N2-metal distance [2.161(5) Å], which are comparable to those in $[(\eta^6-C_6Me_6)RuCl(C_2H4N-2-CH=N=C_6H_4-p-NO_2)]PF_6$, $[(\eta^5-C_5Me_5)RhCl(C_2H4N-2-CH=N=C_6H_4-p-NO_2)]BF_4$, $[(\eta^5-C_5Me_5)RhCl(C_2H4N-2-CH=N=C_6H_4-p-NO_2)]PF_6$, $[(\eta^6-C_6H_6)Ru(2-(2-thiazolyl)-1,8-naphthyridine)Cl]PF_6$, $[(\eta^6-p-iPrC_6H_4Me)RuCl(2,3-bis(2-pyridyl)pyrazine)]BF_4$. While the M-Cl [2.406(2) and 2.396(4)] bond lengths show no significant differences in all the cations and reported values. $[(\eta^6-C_6Me_6)RuCl(C_2H4N-2-CH=N=C_6H_4-p-NO_2)]PF_6$, $[(\eta^5-C_5Me_5)RhCl(C_2H4N-2-CH=N=C_6H_4-p-NO_2)]BF_4$, $[(\eta^5-C_5Me_5)RhCl(C_2H4N-2-CH=N=C_6H_4-p-NO_2)]PF_6$, $[(\eta^6-p-iPrC_6H_4Me)RuCl(2,3-bis(2-pyridyl)pyrazine)]BF_4$. The distances between the ruthenium atom and the centroid of the $((\eta^6-p-iPrC_6H_4Me)RuCl(2,3-bis(2-pyridyl)pyrazine))$ ring is 1.683 Å in complex 2, whereas the distance between the rhodium atom and the centroid of the $((\eta^5-C_5Me_5)RhCl(2,3-bis(2-pyridyl)quinoxaline))$ ring is 1.781 Å in complex 7. These bond distances are comparable to those in the related complex cations $[(\eta^6-p-iPrC_6H_4Me)Ru(pyNp)Cl]PF_6$, $[(\eta^5-C_5Me_5)Ir(pyNp)Cl]PF_6$ (PyNp=2-(2-pyridyl)-1,8-naphthyridine) (1.79 Å)27 and $[(\eta^5-C_5Me_5)Rh(3,6-bis(2-pyridyl)4-phenylpyridazine)Cl]PF_6$ (1.789 Å).

Figure 5.3: Molecular structure of complex $[(\eta^5-C_5Me_5)Rh(bppp)Cl]PF_6$ [7]PF_6. All hydrogen atoms, solvent molecule and anion are omitted for clarity.
5.3.4 Synthesis of the dinuclear complexes 9 to 12 as hexafluorophosphate salts

The reaction of the dimeric chloro complexes \([(\eta^6\text{-arene})\text{Ru(\mu-Cl)}\text{Cl}]_2\) (arene = C\(_6\)H\(_6\), p-Pr\(_2\)C\(_6\)H\(_4\)Me) and \([(\eta^5\text{-C}_5\text{Me}_5)\text{M(\mu-Cl)}\text{Cl}]_2\) (M = Rh, Ir) with 1.5 equiv. of 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (bppp) in methanol results in the formation of the orange color, air-stable dinuclear dicationic complexes \[\{(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}\}_2\text{(bppp)}\]^2+ [9]PF\(_6\), \[\{(\eta^6\text{-p-PrC}_6\text{H}_4\text{Me})\text{RuCl}\}_2\text{(bppp)}\]^2+ [10]PF\(_6\), \[\{(\eta^5\text{-C}_5\text{Me}_5)\text{RhCl}\}_2\text{(bppp)}\]^2+ [11]PF\(_6\) and \[\{(\eta^5\text{-C}_5\text{Me}_5)\text{IrCl}\}_2\text{(bppp)}\]^2+ [12]PF\(_6\). All these complexes are isolated as their hexafluorophosphate salts (Scheme 5.3) and they were characterized by IR, Mass, \(^1\)H-NMR spectrometry and elemental analyses.

Infrared spectra of these dinuclear complexes 9 to 12, showed a similar trend to the mononuclear cationic complexes 1 to 8. In the mass spectra the complexes 7, 8, 11 and 12 hexafluorophosphate salts give rise to two main peaks; a minor peak with an approximately 50% intensity attributed to \([M^{2+} + PF_6]^+\) at m/z 940, 1052, 1058 and 1236 respectively, and a major peak which corresponds to loss of [(arene)MCl]\(^+\) fragment to the formation of mononuclear cations 5-8 at m/z = 580, 637, 739 and 729 respectively.
The $^1$H NMR spectra of the dinuclear cationic complexes 9 to 12 exhibit seven distinct resonances at 9.55 (d, 2H), 9.37 (s, 2H), 9.14 (d, 2H), 8.52 (d, 2H), 8.48 (t, 2H), 8.36 (t, 2H), 7.86 (d, 2H) which are assignable to pyridine, pyrazole and pyridazine ring protons of the 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (bppp) ligand. The chemical shift of the bppp ligand protons upon complex formation shifted down field with reference to free ligand. However $H_{tr}$ protons of metal bounded pyrazoles shifted up field compared to $H_{sg}$ unbound pyridazine protons of bppp ligand up on complexation; this may be due to the metal to ligand charge transfer in all these complexes (Figure 3). Besides these bppp ligand resonances complex 9 exhibit a singlet at $\delta = 5.75$ for the two benzene ring and complex 10 exhibits two doublets at $\delta = 1.18 - 1.12$, and septets at $\delta = 2.68$ for the protons of the isopropyl group and a singlet at $\delta = 2.25$ for the methyl protons of $p$-cymene ring. The four doublets observed at $\delta = 6.10 - 5.54$ correspond to the aromatic $p$-cymene ring CH protons. Interestingly the chemical shift of these protons as well as methyl protons shifted downfield significantly with reference to starting precursor ranging from $\delta = 5.20$ to 5.42 and mono nuclear complexes (figure 5.4).

![Figure 5.4: $^1$H-NMR spectrum of compound 18 in CDCl$_3$, represents bppp ligand resonances and $p$-cymene ligand aromatic protons.](image)
This could be due to the increased steric nature on the p-cymene ring in dinuclear complexes compared to mono nuclear compounds. Complexes 11 and 12 exhibit a strong peak at $\delta = 2.05$ and 1.99 for the protons of pentamethylcyclopentadienyl ligands respectively, which are slightly shifted downfield in comparison to the starting complexes.

5.3.5 UV-Visible spectroscopy

Electronic absorption spectra of compounds pp-Cl, bppp and complexes 1 to 12 were acquired in acetonitrile, at $10^5$ M concentration in the range 220-550 nm. The spectral data are well formulated in experimental section. The spectrum of the ligand 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (pp-Cl) exhibit a band at 318 nm, while ligand 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (bppp) exhibit two bands at 316 nm and 331 nm as a shoulder peak, which are assigned to intra-ligand $\pi \rightarrow \pi^*$ transitions. The electronic spectra of these complexes are characterized by two main features, viz., an intense ligand-localized or intra-ligand $\pi \rightarrow \pi^*$ transition in the ultraviolet region and metal-to-ligand charge transfer (MLCT) $d\pi(M) \rightarrow \pi^*$ (L - ligand) bands in the visible region. Since the low spin $d^6$ configuration of the mononuclear complexes provides filled orbitals of proper symmetry at the Ru(II), Rh(III) and Ir(III) centers, these can interact with low lying $\pi^*$ orbitals of the ligands. All the mononuclear complexes 1 to 4 show only an intense band in the region 308-316 nm, while complexes 5 to 8 shown three bands at 276-278 nm, 312 - 314 nm and a broad peak at 417-423 nm. Where as the dinuclear complexes 9 to 12 show three bands, which are almost similar to complexes 5 to 8 at 274 to 276 nm as a shoulder peak at 312-314 nm as a high intense peak and a broad band at 418 - 420 nm. The high intensity band in UV region for both mononuclear and dinuclear complexes is assigned to inter and intra-ligand $\pi - \pi^*$/$n - \pi^*$ transitions, while the low energy absorption band in the visible region for all complexes is assigned to metal-to-ligand charge transfer (MLCT) ($t_{2g} - \pi^*$). Representative spectra of these complexes are represented in figure 5.5.
5.4 Conclusions

In summary, in this work we have prepared two novel chelating ligands 3-chloro-6-(3-pyridyl-1-pyrazolyl)pyridazine (pp-Cl) and 3,6-bis(3-pyridyl-1-pyrazolyl)pyridazine (bppp). Ligands pp-Cl and bppp reacted with series of arene ruthenium and Cp* rhodium and iridium complexes giving new series of mononuclear and binuclear complexes. However, we were unable to get single crystals of dinuclear complexes, which were characterized by other spectral techniques.

5.5 Supplementary material

References

Pyrazolyl-pyridine analogues

Chapter 5